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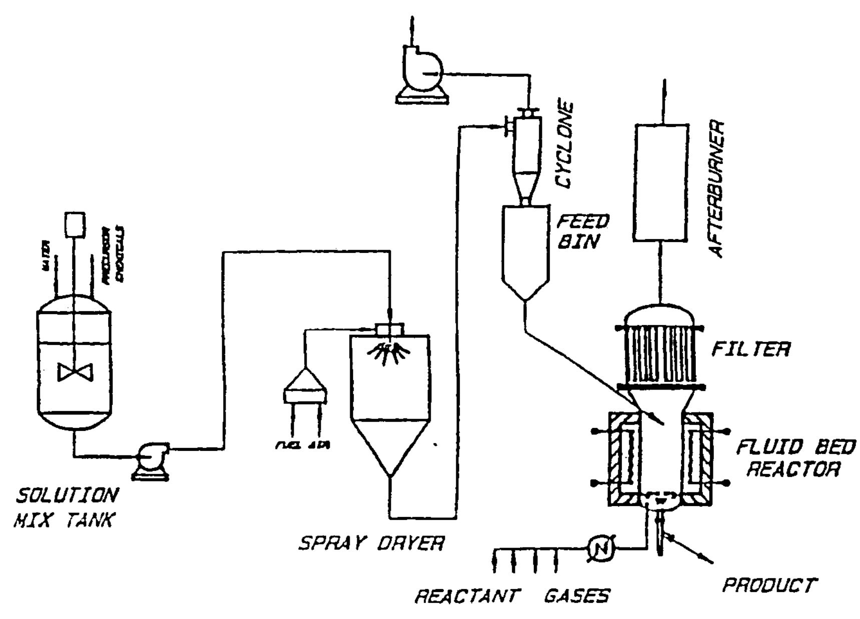

(57) Abstract

A new carbothermic reaction process is described for the thermochemical processing of nanophase WC-Co powders. The process permits shorter reaction times, reduced temperatures, and finer microstructures compared to conventional processing methods. The process builds on our experience with spray conversion processing [1], but involves 1) chemical vapor infiltration reaction of the carbon infiltrant and particle substrate to form WC-Co; and 2) removal of any excess (unreacted) carbon by controlled gasification. A feature of the carbothermic reaction process is its adaptability to conventional WC-Co processing technology, as well as to spray conversion processing technology. The resulting powder particles consist of a network of fine grains, (less than 100 nm) of WC and Co with interconnected fine porosity. Powder particles suitable for subsequent handling and consolidation are readily produced with diameters greater than 10 microns.

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CARBOTHERMIC REACTION PROCESS FOR MAKING NANOPHASE WC-Co POWDERS

This application is a continuation in part of presently pending U.S. application number 741,327 filed on August 7, 1991 which is itself a continuation in part of PCT US90 06550, filed November 2, 1990, itself a continuation in part of U.S. Serial Number 433,742, filed November 9, 1989.

Field of the Invention

The present invention discloses and claims a process for the production of nanophase WC-Co powders by thermochemical conversion of homogeneous chemical precursor powders. The process utilizes a carbothermic reaction process, wherein the precursors are thermochemically converted by controlled gas-solid reactions at unexpectedly low temperatures to the nanophase powder products and results in a substantial decrease in overall reaction times.

Background of the Invention

Presently pending U.S. patent applications number 433,742, filed on November 9, 1989, and the

continuation in part thereof, having Serial No. PCT/US90/06550, filed on November 2, 1990, both being incorporated herein by reference, disclose a new spray conversion process for producing novel nanophase WC-Co composite powders. The process involves three main steps: 1) preparation of starting solutions of mixed salts by wet chemistry methods, 2) spray drying, calcining or roasting of the starting solutions to form homogeneous precursor powders, and 3) thermochemical conversion of the precursor powders to the desired end product powders by controlled gas/solid reactions in a fluid bed reactor. Subsequent consolidation of the powders into useable structural forms may be accomplished by thermal spraying, laser surfacing, cold compaction and sintering, and incipient melt forming.

The thermochemical conversion of the precursor powders according to the process disclosed in these above mentioned patent applications occurs over a period of several hours.

The process disclosed herein, which we refer to as the "carbothermic reaction process," is a modification of the spray conversion process, which permits better control of the WC-Co microstructure at the submicron level and greatly improves conversion efficiency.

The original thermochemical process provided a means for producing nanophase WC-Co composite powders with a composition of 23% by weight cobalt. The steps

are outlined below:

1. An aqueous solution of $CoCl_2$ is mixed with a solution of H_2WO_4 in ethylenediamine (en) to precipitate crystals of $Co(en)_3WO_4$ the prototype precursor compound.

2. The crystalline powders are reductively decomposed to form nanoporous/nanophase W-Co powder (see Figure 1).

3. The high surface area reactive intermediate, W-Co, is converted to WC-Co or other phases by reaction with CO_2/Co gas mixtures (see Figure 2).

The nature of the microstructure of the composite is determined by controlling the temperature of the carburization reaction and the carbon activity of the gas phase. The resulting powder particles have roughly the same size (10 x 100 microns) and morphology (hexagonal prismatic rods) as the original particles precipitated from solution, but within these particles the microstructure is a WC-Co nanophase composite, Figure 3.

Using $Co(en)_3WO_4$ as the precursor compound necessarily fixes the Co/W atom ratio at 50/50 and the resulting WC-Co composition at 23 weight percent Co. This composition is at the low end of WC loadings that are used commercially. Thus, there is a need to extend the compositional range of precursors to include more tungsten. The range of WC-Co compositions of commercial interest is 3-30 weight percent Co.

To overcome this limitation in the original

thermochemical process, we have adopted spray drying of solution mixtures as the preferred method of making precursor powders with a range of compositions. In spray drying the solvent phase is rapidly evaporated in a hot gas stream, leaving solid particles that are homogeneous mixtures. Under ideal conditions the solid particles are amorphous or microcrystalline, with no evidence of phase separation, even when starting from multicomponent solutions.

To summarize, our "Spray Conversion Processing" technology involves:

1. Preparation and mixing of the starting solution. This may take the form of premixing or in situ mixing at the is spray drying nozzle. The latter is favored when chemical reaction between the components can occur.

2. Spray drying, calcining or roasting of the starting solution to form homogeneous spherical precursor particles. These may be amorphous, microcrystalline, or mixed amorphous/microcrystalline in nature.

3. Thermochemical conversion of the precursor particles by controlled gas-solid reaction in a fluid bed reactor. This involves control of reaction time, bed temperature, and gas composition. See Figure 4.

In preparing the precursor powders the preferred starting point is an aqueous solution of ammonium metatungstate (AMT), $(NH_4)_6(H_2W_{12}O_{40})\cdot 4H_2O$ and cobalt nitrate, $Co(NO_3)_2\cdot 6H_2O$.

AMT was chosen because among the polytungstates, it has the highest solubility in water. Water soluble $Co(NO_3)_2 \cdot 6H_2O$ was selected because it decomposes to form non-corrosive NO_x compounds, which are easily scrubbed from the system. Chloride compounds, if used, can cause corrosion of the metal components of the reactor.

The Co/W atom ratio was adjusted to 1.0, 0.63, 0.21, and 0.1 by mixing appropriate quantities of AMT and cobalt nitrate. Spray drying and thermochemical conversion in CO_2/CO gas at a carbonactivity of 0.95 yields the resulting nanophase WC-Co powders having 23, 15, 6, and 3 wt% Co binder phase, respectively. The particle microstructure of these powders was substantially the same as that obtained for WC-Co composite made from $Co(en)_3WO_4$ powder.

The thermochemical conversion of precursor powders in a fluid bed reactor has been a substantial improvement in the technology. While one can obtain sufficient powder for characterization purposes using a laboratory-scale fixed bed reactor, it is not easy to obtain the larger quantities needed for mechanical property evaluations, much less produce commercial quantities of powders for field testing. The difficulty has been circumvented by adopting an industrial-scale fluid bed reactor as the means for controlled thermochemical conversion of the precursor powder to WC-Co nanophase composite powder. A fluid bed reactor is ideal for thermochemical conversion of the precursor

powder because of the uniform bed temperature and constant gas/solid environment throughout the bed.

As noted above, a large excess of carbon is deposited in the powder bed when pure CO is used as a carbon source gas. This excess carbon is removed by gasification, using a CO/CO_2 mixture of low carbon activity in a final processing step. Complete removal of the uncombined carbon is extremely important because such carbon impurity contributes to porosity in parts that are made from WC-Co powder by liquid phase sintering. If CO/H_2 is used as the carbon source gas, the build up of uncombined carbon is reduced. As shown in figure 8, if the carbon concentration is set below 60%, the deposition of uncombined carbon is slowed. At CO concentrations below about 20%, the carburization reaction stops at the W_2C stage without further carbon build up. At CO concentrations of about 30% to 40%, WC is formed in the carburization reaction and uncombined carbon only builds very slowly. This slow build up of uncombined carbon is of great practical importance because it limits the amount of carbon needed to be removed in the final processing step.

The avoidance of uncombined carbon build-up can be rationalized in the following manner. Presumably both CO and H_2 dissociate on the surface of the metallic alloy intermediate thereby providing a population of surface carbon, oxygen, and hydrogen atoms. A surface carbon atom can easily diffuse into the alloy and react

with W to form WC. However, if the diffusion of the carbon atom is blocked or slowed as the WC concentration builds, the surface carbon atom can be gasified by combining with surface hydrogen atoms to form CH_4. Similarly, a surface oxygen atom can be gasified by reaction with surface hydrogen atoms to form water. In effect, H_2 keeps the surface of the powder clean as the W-CO powder is carburized to WC-Co powder.

Brief Description of the Drawings

Figure 1 is a graph depicting the reductive decomposition of $Co(en)_3\ WO_4$ powder.

Figure 2 is a graph showing the conversion of W-Co to nanophase WC-Co powder by carburization.

Figure 3 is a photomicrograph showing the morphology of WC-Co powders prepared from $Co(en)_3\ WO_4$ powder.

Figure 4 is a flow diagram of the spray conversion process.

Figure 5 is a thermogravimetric analysis trace of the carbothermic reaction synthesis of WC-10 wt % Co.

Figure 6 are photomicrographs of the microstructures of converted powders.

Figure 7 depicts line broadening of the (100) WC diffraction peak from WC-10 wt% Co powder produced by carbothermic reaction at 700, 750, 800, and 850ºC.

Figure 8 depicts carbon pick up during the carbonization step of the carbothermic process using CO/H_2 mixtures as the carbon source gas.

Summary of the Invention

An object of the present invention is to provide a method for producing nanoscale microstructures of WC-Co at reduced reaction temperatures and reduced reaction times, and the use of an external carbon bed as a CO regenerator for a more efficient process.

It is a further object to provide a method for producing nanoscale microstructures of WC-Co powder.

We have improved the conversion efficiency and reduced the microstructural scale by our new improvements in the technology, which we call carbothermic reaction processing. Until recently all thermochemical conversions were conducted in CO_2/Co gas mixture with carbon activities in the range .35 to .95. In all cases, the rapid initial uptake of carbon gives rise to a metastable phase, prior to its conversion to the thermodynamically stable WC-Co composition. This has two consequences. First, the metastability of the intermediate phase or phases prolongs the overall conversion time and increases the cost. Second, the longer reaction time permits particle coarsening and limits the ultimate microstructural scale attainable. For example, if reduction of the precursor powder yields a nanophase mixture of W and Co, the carburization step may result in the coarsening of the microstructure from 0.01 to 0.3 microns. Even coarser

microstructures can be generated by carburization at higher temperatures.

However, we have discovered that the rapid carbon uptake in the first stage of carburization is the key to reducing the microstructural scale of the WC-Co powder. Such uptake of carbon occurs at unexpectedly low temperatures, apparently because of catalytic decomposition of CO by the cobalt phase. This phenomenon can be exploited to deposit amorphous carbon within the nanopores of the W-Co particles at low temperatures. The high dispersion of carbon throughout the W-Co particles and the short diffusion distances accelerate the conversion to WC-Co, while preserving the desirable ultrafine microstructure. Thus, the microstructure can easily be reduced below 0.1 micron and there is the potential for achieving .01 micron or less in WC grain size.

We have also discovered that a substantial decrease is conversion time is realized by carburizing at an activity in excess of 1.0 and then completing the conversion at a carbon activity below 1.0, preferably about 0.5. In the examples set forth below, we will show that reaction times can be as low as 45 minutes. This amounts to a tenfold and greater decrease in time compared to the time necessary to effect total carburization of the powders converted according to our previously disclosed processes. In those processes the carbon activity

was held substantially constant throughout the entire carburization process.

In practice, the amount of carbon introduced exceeds the stoichiometric requirement for the complete conversion to WC-Co. This fixes the carbon activity during the reaction to 1.0, thereby producing the maximum reaction rate. After the conversion reaction is complete, the excess uncombined or free carbon is removed by introducing a CO_2/Co gas mixture of about 0.5 carbon activity, depending on the reaction temperature.

Figure 5 shows a typical thermogravimetric analysis trace of such a carbothermic reaction treatment at 800°C. It is evident that the rapid carbon uptake greatly reduces the formation of a metastable intermediate phase and promotes the formation of WC-Co.

With reference to Figure 5, during the first phase of carburization, corresponding to the addition of CO gas, carbon activity equals or exceeds 1.0. The CO gas undergoes catalytic decomposition and carbon precipitates on and is dispersed throughout the W-Co particles. The ultrafine microstructure is preserved during the time when carbon precipitation results in an almost one hundred percent increase in particle weight, as is indicated at the twenty minute mark of carburization

Excess unreacted carbon is then removed by lowering the carbon activity to approximately 0.5 by altering the atmosphere to a CO/CO_2 mixture, wherein excess carbon reacts with C02 to form carbonmonoxide:

$$C + CO_2 \rightarrow 2\ CO$$

Carbon is removed, resulting in a rapid weight reduction which levels off approximately 20 minutes after reducing the carbon activity (or 40 minutes after initiating carburization). By means of thermal gravimetric analysis, the practitioner of the invention can determine the time at which to reduce the carbon activity and ultimately the time at which the carburization process is completed.

Figure 6 shows the corresponding microstructure of the converted powder with WC grain size between 30-100 nm. Further is evidence for the grain size reduction with decreasing reaction temperature is shown in Figure 7. It is seen that the 100 peak is both broadened and shifted as the synthesis temperature decrease and the grain size gets smaller.

The processes disclosed herein are compatible with existing conventional technologies for producing WC-Co powders, which involves the following sequence of steps:

1. A tungsten containing powder, usually ammonium paratungstate, is spread as a thin layer on graphite trays. The trays are placed in a muffle furnace where the salt is reduced to tungsten powder by a reducing gas.

2. The tungsten powder is removed from the furnace and mixed with carbon powder.

3. The mixture is again spread on the graphite trays, which are returned to the furnace where the tungsten reacts with the carbon at high temperature (1400-1600 C) to form WC powder.

4. The WC powder is removed from the furnace and ball milled with Co powder in order to coat the WC particles with Co.

5. The WC-Co powder is combined with a binder, usually paraffin or polyethylene glycol, and spray dried to form a spherical grade powder. The binder acts as a die-wall lubricant in cold compaction of preforms prior to liquid phase sintering.

A novel variation of the conventional commercial process discussed above is to introduce carbothermic reaction processing as the means to produce WC-Co powder in a single step. Suitable equipment would include a muffle furnace. The homogeneous spray dried composite precursor powder, which might be prereduced or preoxidized and possibly carbon infiltrated, is spread on the graphite trays and further reaction processing is effected in the muffle furnace by setting the carbon activity of the reaction atmosphere by controlling the amount of CO and CO_2 entering the furnace and by further controlling the furnace temperature. A person skilled in the art would recognize that minimizing bed thickness enhances the addition or removal of carbon into or out of the particles so that mass transfer occurs uniformly throughout the bed. Not only

does this process eliminate mechanical mixing steps (ball milling), it results in a WC-Co mixture of greater homogeneity, permits the carburization reactions to occur at much lower temperatures, and shortens the overall reaction times. Low reaction temperatures and short reaction times favor the formation of the finest microstructures.

A novel variation of the carbothermic process discussed above is to introduce carbon in the precursor solution, either as a fine dispersion or as a compound that can be readily carbonized (such as sucrose), rather than from the gas phase. Our experience with this variation has been that satisfactory carburization can be accomplished at reasonable reaction rates only at temperatures greater than 950°C. This is because solid-solid reactions are not as fast as gas-solid reactions, making it harder to develop and maintain nanostructures. A concern with gas-solid reactions is the large amount of CO gas required to carburize W to WC; two moles of CO are required to produce one mole of WC. In the preferred embodiment of the carbothermic process, outlet gas that is rich in CO_2 gas is recycled through an external hot bed of carbon where CO_2 is converted back to CO. Thus, in this closed loop system carbon is transported in the gas phase from an external carbon source to the fluid bed reactor where the carburization of W occurs. An advantage of this process variation is the ability to independently control the

temperature of the external carbon bed and that of the fluid bed reactor, which allows an increased degree of control compared to the case where carbon is supplied as a fine dispersion in the precursor powder.

The process discussed above shall now be set forth in greater detail with reference to the following examples.

Examples

Examples 1-3 describe preparation of suitable precursor compounds. Examples 4-8 were carried out in a thermogravimetric analyzer. Similar results were obtained on gram-scale quantities of powder in a tube furnace (fixed bed reactor). Examples 9-11 were carried out on kilogram-scale quantities of powder in 4", 6" or 14" diameter fluid bed reactors.

Example 1

WC-23% Co from crystalline $Co(en)_3WO_4$ precursor powders. An aqueous solution of $CoCl_2$ was combined with a solution of H_2WO_4 in ethylenediamine to precipitate crystalline $Co(en)_3WO_4$. Low concentrations of the reactants in these solutions produce hexagonal rods (20x100 microns) while high concentrations produced flat plates (20x5x1 microns). When $Co(en)_3WO_4$ solution is spray dried the resulting microcystalline particles are spherical, and after fluid bed conversion to WC-Co, have microstructures that are identical to those obtained from the single crystal particles.

Example 2

The use of WC-Co from amorphous/microcrystalline $Co(en)_3WO_4$ crystalline precursor, prepared under near equilibrium conditions by precipitation from solution, necessarily fixes the Co:W ratio at 1:1, which results in WC-23% Co powder after fluid bed conversion. In order to achieve a wider range of WC-Co compositions it is necessary to prepare homogeneous mixtures of $Co(en)_3WO_4$ with another source of W, e.g. H_2WO_4. This can be accomplished by rapid spray drying of mixtures of $Co(en)_3WO_4$ (solution A) and H_2WO_4 in aqueous NH_4OH (solution B) . For example, the Co/W ratio may be adjusted to the values of 1.0, 0.63, 0.21, and 0.1 by mixing appropriate quantities of solutions A and B. When these solutions are spray dried in a laboratory spray dryer fitted with a 2" rotary atomizer spinning at 35000 rpm; inlet and outlet temperatures 205 and 115°C, respectively; and a starting solution feed rate of 156 ml/min the resulting powders are amorphous or microcrystalline, depending on the Co/W ratio in the starting solution.

Example 3

WC-Co from amorphous AMT-$CoCl_2$ precursor powders.

An alternative precursor solution, which is preferred solution, involves the use of ammonium metatungstate (AMT) and $CoCl_2 \cdot 6H_2O$ or $Co(NO_3)_2 \cdot 6H_2O$ or $Co(CH_3COO)_2 \cdot 4H_2O$. The use of AMT is advantageous because of its high solubility in water and its commercial availability.

Solution C was prepared by dissolving AMT and $CoCl_2 \cdot H_2O$ or $Co(NO_3)_2 \cdot 6H_2O$ or $Co(CH_3COO)_2 \cdot 4H_2O$ in water. The Co:W ratio was fixed at 0.37, which yields 10% Co in the final WC-Co composite powder.

The starting solution was spray dried in a laboratory spray dryer fitted with a pressure nozzle atomizer (80 PSI). The inlet and outlet temperatures were maintained at a nominal 220 and 130°C. The feed solution was pumped into the dryer at 220 ml/min. SEM micrographs of the dried powder showed spherical particles, which were shown to be amorphous by X-ray diffraction.

<u>Example 4. Process at 850°C</u>

A 100 mg sample of AMT/$CoCl_2$ precursor powder, of a composition suitable for making WC-10 wt% Co, was reduced in flowing (90 cc/min) Ar/H_2 (2:3) for 45 minutes to yield 66 mg of porous nanophase W-Co.

Carbon infiltration was achieved using flowing CO (90 cc/min). The carbon uptake resulted in a weight increase to 76 mg in a 20 minute interval. During the next 24 minutes in a flowing CO/CO_2 stream ($a_c = 0.5$) the carburization reaction was completed and the excess free carbon was removed. The final nanophase WC-Co powder sample weight was 70 mg.

<u>Example 5. Process at 800°C</u>

A 100 mg sample of AMT/$CoCl_2$ was converted to nanophase WC-Co powder, as in Example 1, but with a processing temperature of 800ºC; Ar/H_2 reduction for 45

minutes; carbon infiltration for 20 minutes; and carburization and free carbon removal for 24 minutes.

Example 6. Process at 750ºC

A 100 mg sample of AMT/$CoCl_2$ was converted to nanophase WC-Co powder, as in Example 1, but with a processing temperature of 750ºC; Ar/H_2 reduction for 90 minutes; carbon infiltration for 20 minutes; and carburization and free carbon removal for 90 minutes.

Example 7. Process at 700ºC

A 100 mg sample of AMT/$CoCl_2$ was converted to nanophase WC-Co powder, as in Example 1, but with a processing temperature of 700ºC; Ar/H_2 reduction for 150 minutes; carbon infiltration for 35 minutes; and carburization and free carbon removal for 265 minutes.

Example 8. Process at 700/800ºC

A 100 mg sample of AMT/$CoCl_2$ was converted to nanophase WC-CO powder, as in Example 1, but with Ar/H_2 reduction for 150 minutes at 700ºC; carbon infiltration in CO for 35 minutes at 700°C; heating to 800°C in 10 minutes in flowing CO; and simultaneous carburization and free carbon removal in CO/CO_2 for 25 minutes at 800ºC.

Example 9. Process at 750ºC

A 890 g sample of spray dried AMT/$Co(NO_3)_2nH_20$ precursor powder, of a composition suitable for making WC-10 wt% Co, was charged into a 4" diameter fluid bed reactor. The precursor powder was fluidized in N_2 gas at a velocity of 130 ft/min while the temperature was increased from room temperature to 700ºC in 10

minutes. At 700ºC the fluidization velocity was decreased to 60ft/min and the fluidization gas was changed to N_2/H_2 (cracked NH_3) in a 1:3 ratio while the temperature was raised to 750ºC. The precursor powder was reduced at this temperature for 110 minutes to form a nanophase W/Co composite powder. Next the fluidization gas was changed to pure CO at 30 ft/min for 100 minutes. During this period the W/Co particles were carburized to nanophase WC/Co and the bed temperature increased briefly to 800ºC due to the exothermic reaction. The 100 minute reaction time was required to completely eliminate all traces of $M_{12}C$ impurity. After completion of the carburization reaction, excess carbon was removed by fixing the carbon activity at 0.4 at 750ºC in a fluidizing gas mixture of CO/CO_2 (30 ft/min). All excess carbon was removed after 170 minutes and the reactor was allowed to cool to room temperature in a flow of N_2 at 10 ft/min. X-ray analysis showed that the product was free of $M_{12}C$ and thermogravimetric analysis comfirmed the absence of uncombined carbon. The x-ray line broadening was consistent with a WC grain sizes on the order of 20 nm.

Example 10, Process at 750ºC

A 1.6 kg sample of spray dried AMT/$Co(NO_3)_2 6H_2O$ precursor powder, of a composition suitable for making WC-16 wt% Co, was charged into a 6" diameter fluid bed reactor. The precursor powder was fluidized in N_2 gas at a velocity of 130 ft/min while the temperature was increased from room temperature to

700ºC in 20 minutes. At 700ºC the fluidization velocity was decreased to 60 ft/min and the fluidization gas was changed to N_2/H_2 (cracked NH_3) in a 1:3 ratio while the temperature was raised to 750ºC. The precursor powder was reduced at this temperature for 120 minutes to form a nanophase W/Co composite powder. Next the fluidization gas was changed to pure CO at 30 ft/min for 100 minutes. During this period the W/Co particles were carburized to nanophase WC/Co and the bed temperature increased briefly to 800ºC due to the exothermic reaction. The 100 minute reaction time was required to completely eliminate all traces of $M_{12}C$ impurity. After completion of the carburization reaction, excess carbon was removed by fixing the carbon activity at 0.4 at 750ºC in a fluidizing gas mixture of CO/CO_2 (30 ft/min). All excess carbon was removed after 180 minutes and the reactor was allowed to cool to room temperature in a flow of N_2 at 20 ft/min. X-ray analysis showed that the product was free of $M_{12}C$ and thermogravimetric analysis confirmed the absence of uncombined carbon. The x-ray line broadening was consistent with a WC grain sizes on the order of 20 nm.

Example 11. Process In 14" Diameter Fluid Bed Reactor

A 14" diameter fluid bed reactor was equipped with a mechanical agitator to aid in the fluidization of a large powder charge, and with a gas preheater and freeboard heater to facilitate its isothermal operation. The reactor was preheated to 370ºC (nominal) before a 32 kg sample

of spray dried and precalcined precursor powder, suitable for making WC-11 wt% Co powder, was added to the reactor. The powder was added incrementally to the reaction vessel via a double-ball-valve feed lock over a one hour 10 period. Nitrogen gas was kept flowing in the vessel during the powder addition. The precursor powder was reduced in 1:1 N_2:H_2 gas as the reactor was heated from 635ºC to 750ºC (nominal) over a period of two hours. Carbon was added to the powder at 750ºC (nominal) for two hours using CO gas. Excess carbon was removed is from the powder over a four hour period using a CO_2/Co gas mixture. Because of insufficient gas preheating, the reactor could not be operated isothermally. Thus, during the critical final decarburization step of the process, the carbon activity varied between 0.3 and 0.7 due to temperature gradients within the reactor. This processing produced a pyrophoric WC-Co powder, which was passivated using N_2/air mixtures. 25 kg of nanostructured WC-11 wt% Co powder was produced. Example 12 was carried out on kilogram-scale quantities of powder in a fixed bed tubular reactor.

Example 12 Process at 775ºC in a Fixed Bed Reactor

Approximately 2.8 Kg. of precursor powder, which was prepared by calcining spray dried AMT/Co $(NO_3)_2nH_20$ powder, was distributed on two stainless steel trays to form powder beds approximately 1/2 inch deep, 4 inches wide, and 40 inches long. The trays were stacked and inserted into a stainless steel tubular reactor. The powder was

reduced in flowing hydrogen (15 liters/min) for 6 hours at 775ºC. The powder was carburized at 775ºC in 35% CO in H^2 (21.6 liters/min) for 2 hours followed by 1/2 hour in CO/CO_2 (23 liters/min) at a carbon activity of 0. 5. This "carburization cycle" was repeated 5 times. X-ray analysis of the WC-Co powder, so produced, showed the powder to be free of WO_2 and $M_{12}C$ impurities. TGA analysis showed total uncombined carbon to be less than 0.25%. A short final treatment in CO/CO_2 reduced the uncombined carbon level to less than 0.01%. The process yielded approximately 2Kg of nanostructured WC-Co powder.

We Claim:

1. A carbothermic reaction process for the production of nanophase metal/metal-carbide particles comprised of the steps of:

a) obtaining porous precursor particles which act as substrates for carbon infiltration;

b) infiltrating the porous precursor particles with carbon from a carbon source gas at a carbon activity greater than or equal to 1.0, the carbon gas source being selected to avoid an excess accumulation of uncombined carbon on the precursor powders; and

c) simultaneously reacting the carbon and the source gas with the porous precursor powder particle substrates to form at least one carbide phase.

2. The process as set forth in claim 1 further comprised of removing remaining unreacted carbon by gasification using a gas or gas mixture with carbon activity less than 1.0.

3. The process as set forth in claim 1 wherein the precursor powder is obtained by subjecting a solution of metal ions, prepared by dissolution of metals or metal compounds, to a drying treatment selected from the group consisting of spray calcining, spray roasting, spray drying, or freeze drying.

4. The process as set forth in claim 3 wherein the precursor powder is further prepared by a partial or full chemical reduction.

5. The process as set forth in claim 3 wherein the precursor powder is further prepared by a partial or full oxidation.

6. The process as set forth in claim 1 wherein the infiltration with carbon from a carbon source gas is achieved with gases selected from the group consisting of CO, CO/CO_2, CO/H_2, CH_4/H_2 or other gases and gas mixtures capable of achieving carbon deposition and having a carbon activity greater than or equal to 1.0; and preferably using a carbon gas source regenerator.

7. The process as set forth in claim 6 wherein the infiltration of the porous precursor powder particle with carbon is achieved using low temperature catalytic decomposition of the selected gas or gas mixture by the precursor powder particle substrate.

8. The process as set forth in claim 2 wherein the removal of unreacted carbon is effected by a gasification reaction achieved with gases selected from the group consisting of CO_2, CO/CO_2, CO/H_2 CH_4/H_2, or other gases and gas mixtures capable of removing carbon and having a carbon activity less than 1.0.

9. The carbothermic reaction process as set forth in claim 2 wherein the process is effected in a furnace selected from the group consisting of a tube furnace, a muffle furnace, a belt furnace, a rotary kiln, a fluid bed furnace, or any other furnace suited for achieving infiltration of carbon from a carbon source gas at a carbon activity greater than or equal to 1.0 and removal of unreacted carbon by gasification using a gas or gas mixture having a carbon activity less than 1.0.

10. The process as set forth in claim 1 wherein the nanophase metal/metal-carbide particles produced are WC-Co composites.

11. The process as set forth in claim 3 wherein the solution of metal ions is prepared from tungsten and cobalt compounds.

12. The process as set forth in claim 11 wherein the tungsten and cobalt compounds are ammonium metatungstate and cobalt nitrate, and the solution is aqueous.

13. A carbothermic reaction process for the production of nanophase metal/metal-carbide particles comprised of the steps of:

a) preparing porous precursor particles by partial or full chemical reduction, said porous precursor powders acting as substrates for carbon infiltration, the preparation of precursor powder being obtained by subjecting a solution of metal ions prepared from tungsten or cobalt compounds to a drying treatment selected from the group consisting of: spray calcining, spray roasting, spray drying, or freeze drying;

b) infiltrating the porous precursor particles with carbon from a carbon source gas at a carbon activity greater than or equal to 1.0, said carbon source gas being selected from the group consisting of CO, CO/CO_2, CO/H_2, CH_4/H_2, and other gases or gas mixtures capable of achieving carbon deposition and having a carbon activity greater than or equal to 1.0, the carbon gas source being selected to avoid an excess accumulation of uncombined carbon on the precursor powders; said infiltrating of the porous precursor powders being achieved using low temperature

catalytic decomposition of the selected gas or gas mixture by the precursor powder particle substrate;

c) simultaneously reacting the carbon from the source gas with the porous precursor powder particle substrates to form at least one carbide phase;

d) removing remaining unreacted carbon by gasification using a gas or gas mixture of carbon activity less than 1. 0, the gas or gas mixture being selected from the group consisting of CO_2, CO/CO_2, CO/H_2, CH_4/H_2 or other gases or gas mixtures capable of removing carbon and having a carbon activity less than 1.0; the carbon gas source being selected to avoid an excess accumulation of uncombined carbon on the precursor powders, and

said infiltrating and removing process steps being effected in a furnace selected from the group consisting of a tube furnace, a muffle furnace, a belt furnace, a rotary kiln, a fluid bed furnace, or any other furnace suited for achieving infiltration of carbon from a carbon source gas at a carbon activity greater than or equal to 1.0 and removal of unreacted carbon by gasification using a gas or gas mixture having a carbon activity less than 1.0.

14. The process as set forth in claim 13 wherein the tungsten and cobalt compounds are ammonium metatungstate and cobalt nitrate and the solution is aqueous.

15. The nanophase powder particle produced according to claim 1.

16. The nanophase WC-Co powder particle produced according to claim 10.

17. The nanophase powder particle produced according to claim 11.

18. The nanophase powder particle produced according to claim 12.

19. The nanophase powder particle produced according to claim 13.

20. The nanophase powder particle produced according to claim 14.

21. A carbothermic reaction process for the production of nanophase metal/metal-carbide particles comprised of the steps of:

a) obtaining porous precursor particles having surfaces. said particles acting as substrates for carbon infiltration;

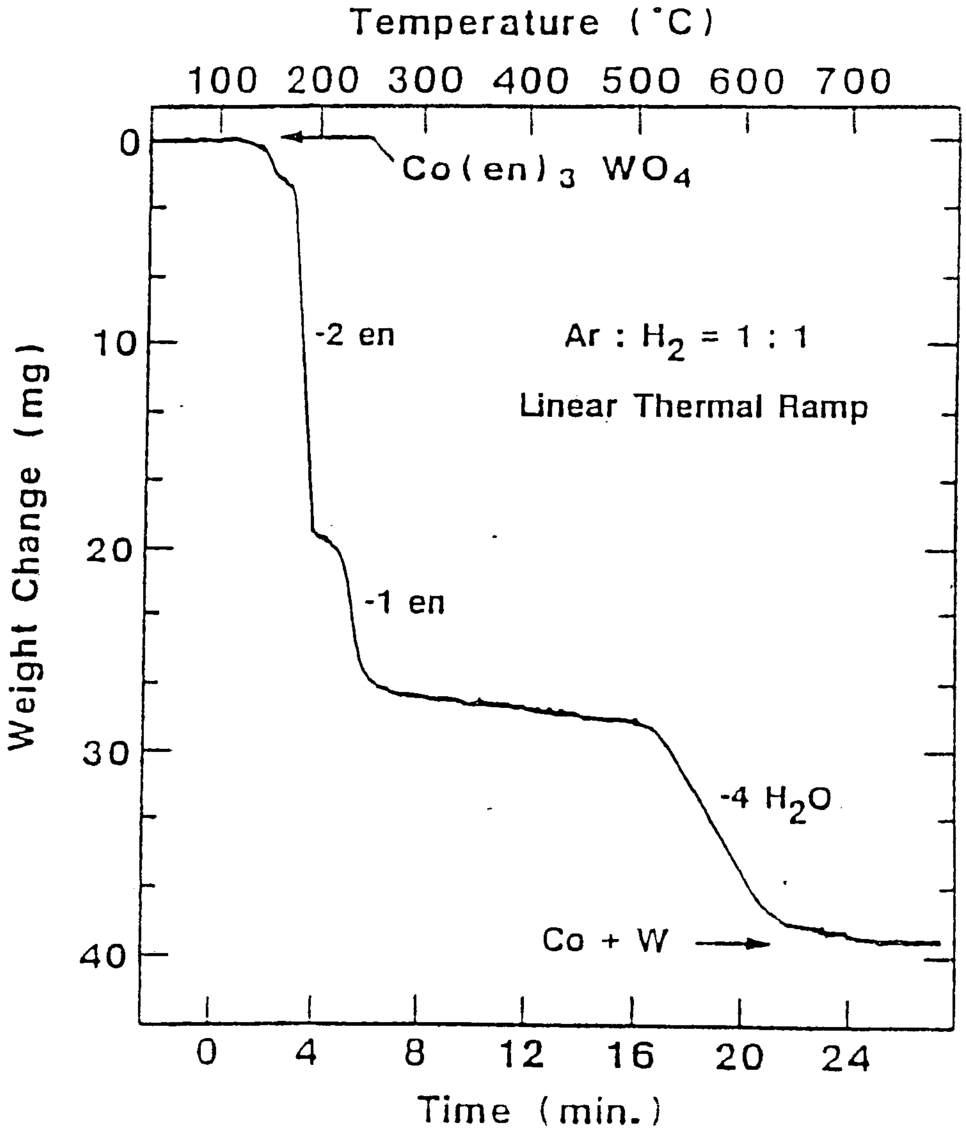
b) infiltrating the porous precursor particles with carbon from a carbon source gas at a carbon activity greater than or equal to 1.0 so that the carbon from the source gas reacts with the porous precursor powder particle substrates to form at least one carbide phase, said carbon source gas being introduced to the porous precursor particles in combination with a second gaseous component capable of combining with carbon or an atomic constituent of the carbon source gas which is deposited at the surfaces of said particles but has not reacted with or diffused into particles.

22. A carbothermic reaction process for the production of nanophase metal/metal-carbide particles exhibiting a relatively lesser content of free, unreacted carbon and other impurities, comprised of the steps of:

a) obtaining porous precursor particles having surfaces, said particles acting as substrates for carbon infiltration;

b) infiltrating the porous precursor particles with carbon from a carbon source gas at a carbon activity greater than or equal to 1.0 so that the carbon from the source gas reacts with the porous precursor powder particle substrates to form at least one carbide phase, said carbon source gas being introduced to the porous precursor particles in combination with a second gaseous component capable of reacting with carbon or an atomic constituent of the carbon source gas which is deposited at the surfaces of said particles but has not reacted with or diffused into particles so that the reacting of the second gaseous component with the carbon or the second atomic constituent of the source gas results in the removal of impurities from the surface of the precursor particles, effecting a nanophase metal/metal-carbide particle relatively free

of free, unreacted carbon and other impurities.



Temperature (°C)
100 200 300 400 500 600 700
Weight Change (mg)
0
10
20
30
40
Co(en)3 WO4
-2 en
Ar : H2 = 1 : 1
Linear Thermal Ramp
-1 en
-4 H2O
Co + W
0 4 8 12 16 20 24
Time (min.)

FIG. 1

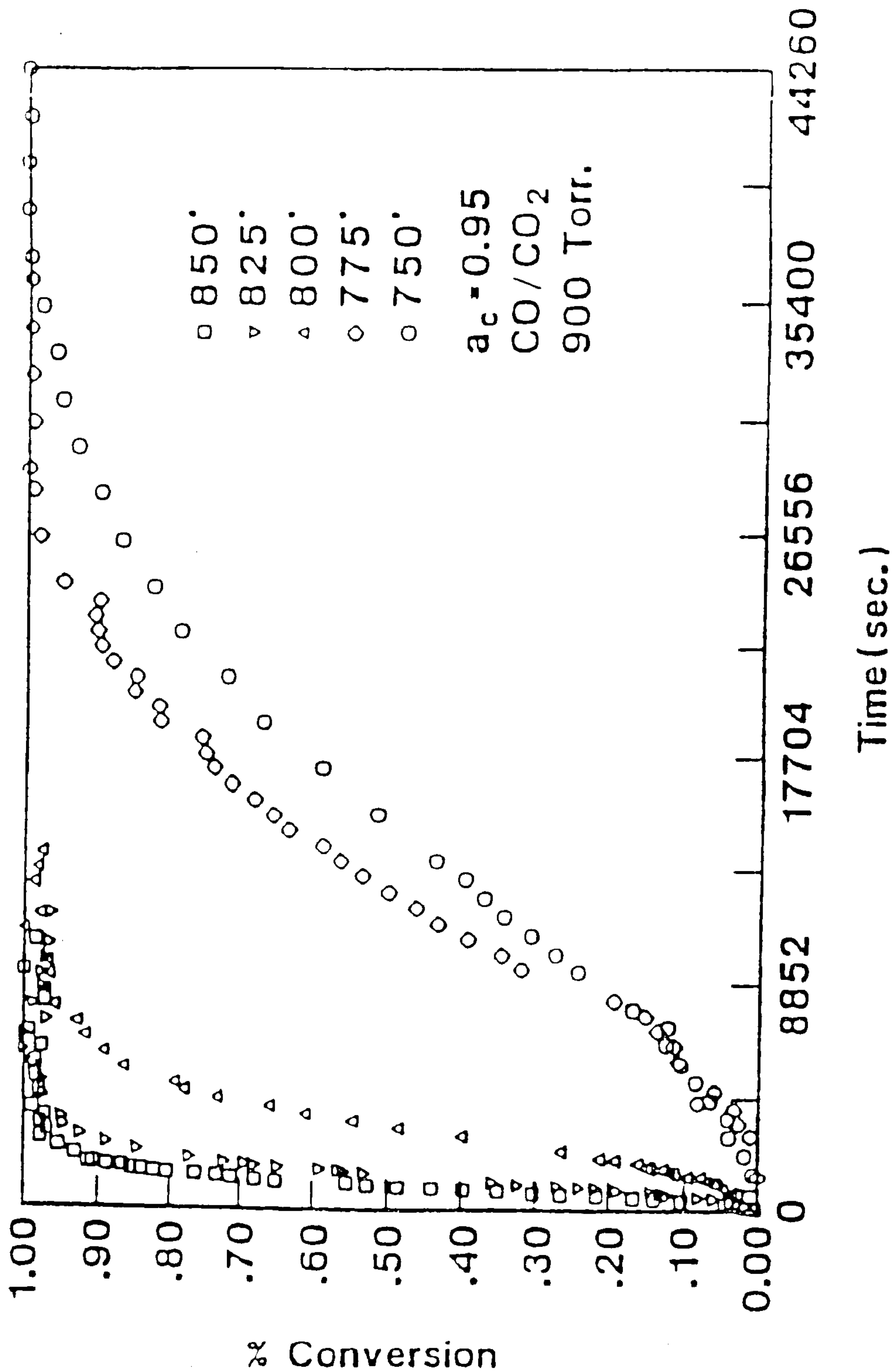
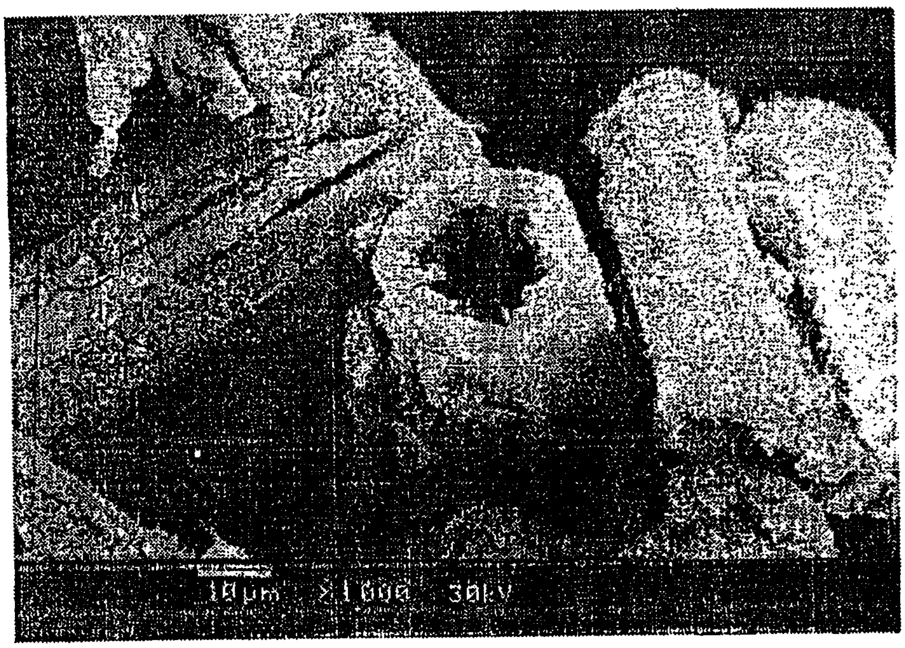

850°
825°
800°
775°
750°
a_c = 0.95
CO/CO2
900 Torr.
Time (sec.)
0
8852
17704
26556
35400
44260
% Conversion
1.00
.90
.80
.70
.60
.50
.40
.30
.20
.10
0.00

FIG. 2

FIG. 3



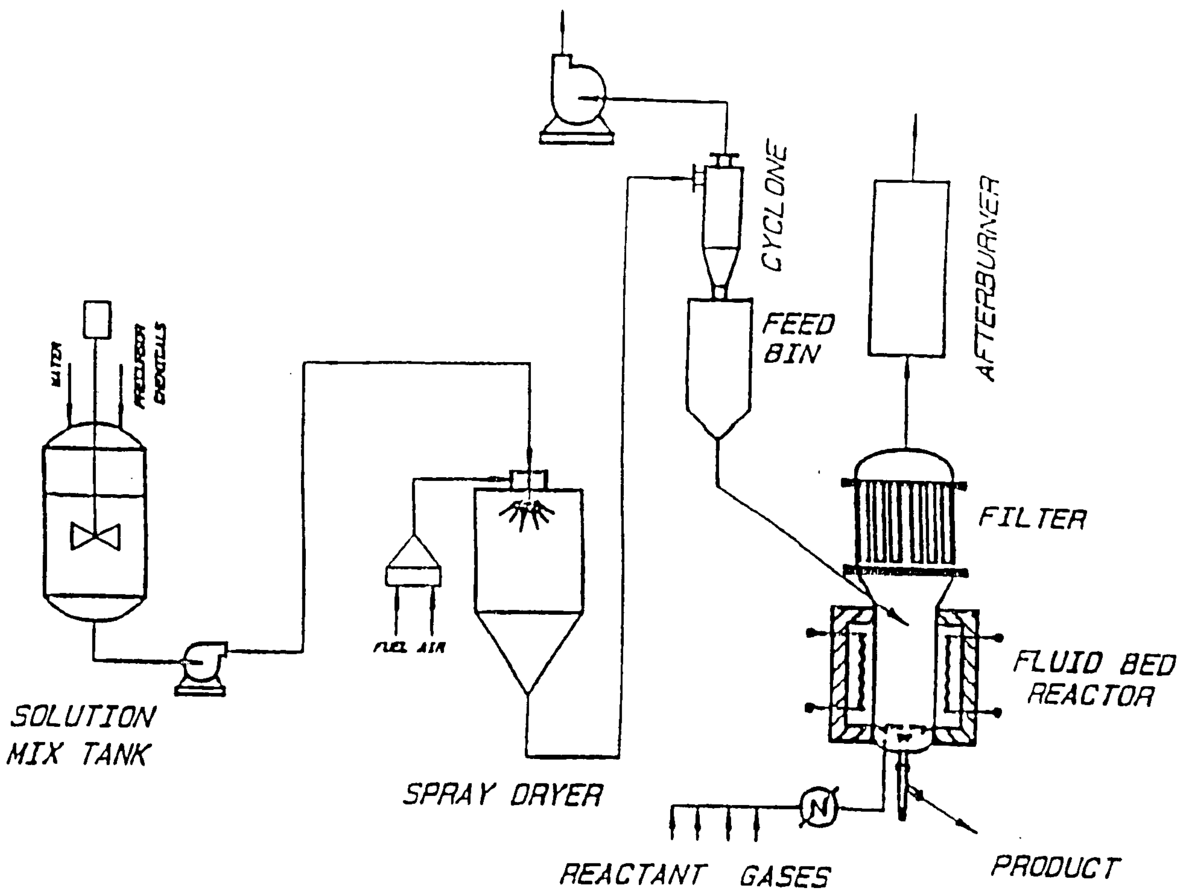
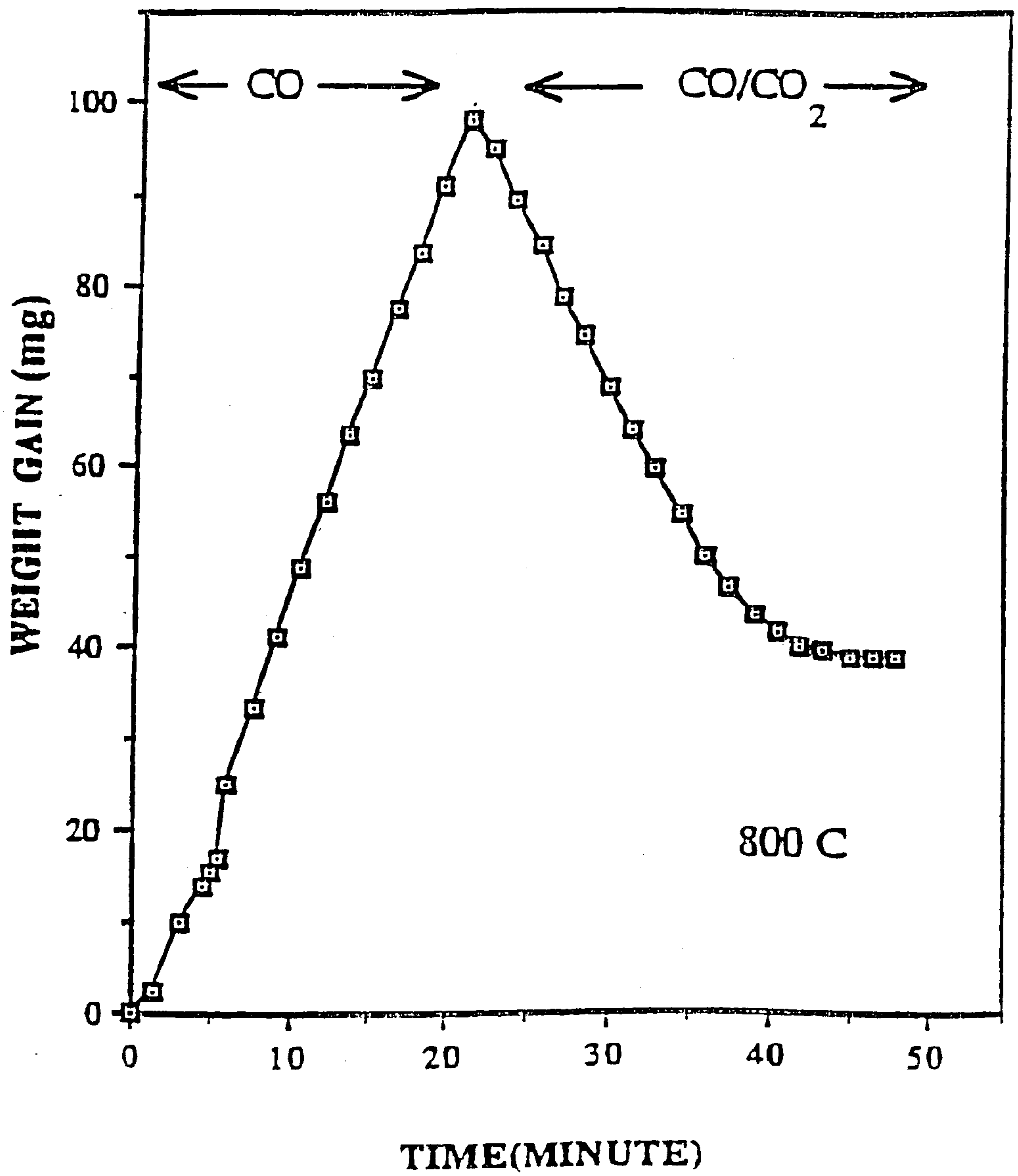

CYCLONE
AFTERBURNER
FEED BIN
FILTER
FUEL AIR
FLUID BED REACTOR
SOLUTION MIX TANK
SPRAY DRYER
REACTANT GASES
PRODUCT

FIG. 4

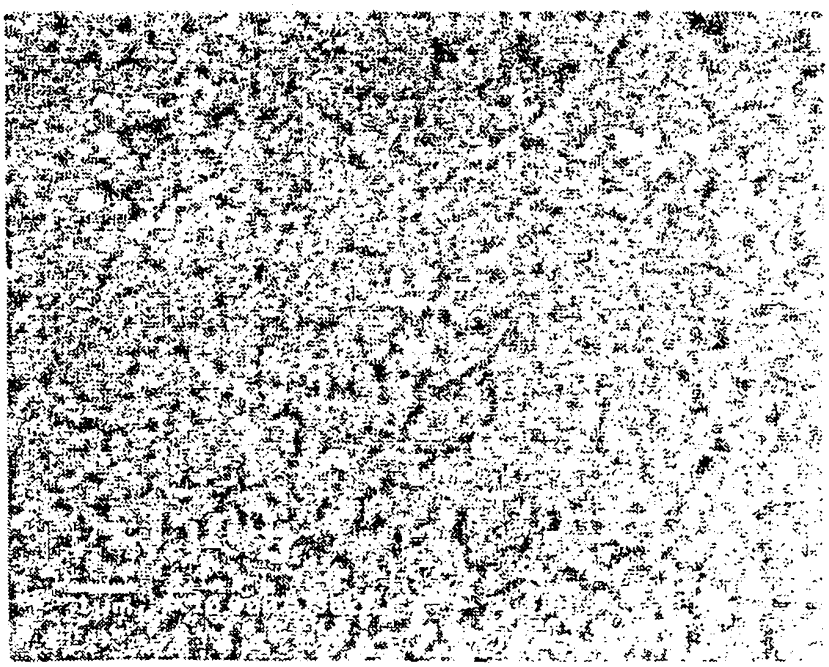


CO
CO/CO2
100
80
60
40
20
0
WEIGHT GAIN (mg)
800 C
0
10
20
30
40
50
TIME(MINUTE)

FIG. 5

FIG. 6A

FIG. 6B



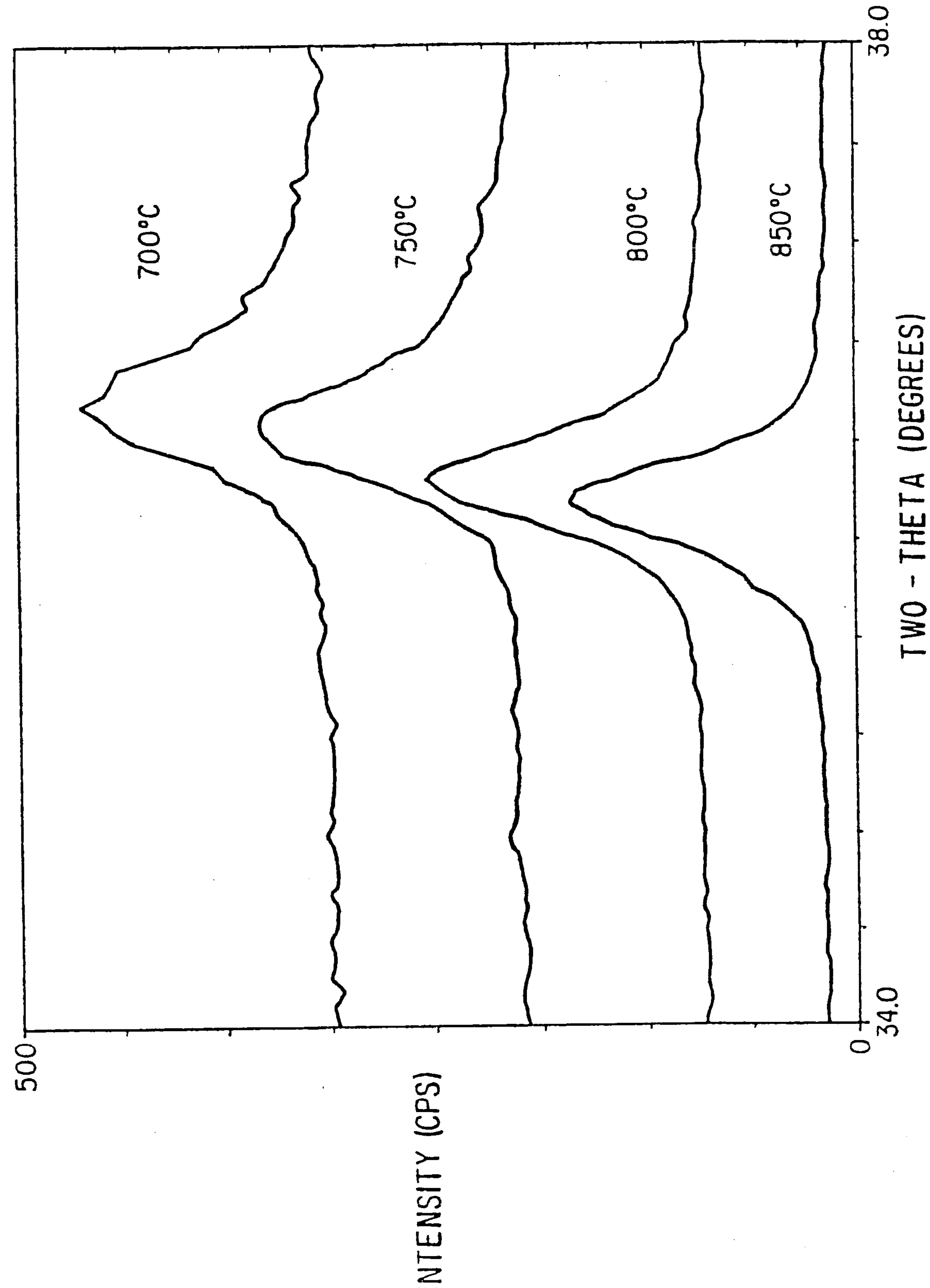

700°C
750°C
800°C
850°C
500
0
INTENSITY (CPS)
34.0
38.0
TWO - THETA (DEGREES)

FIG. 7

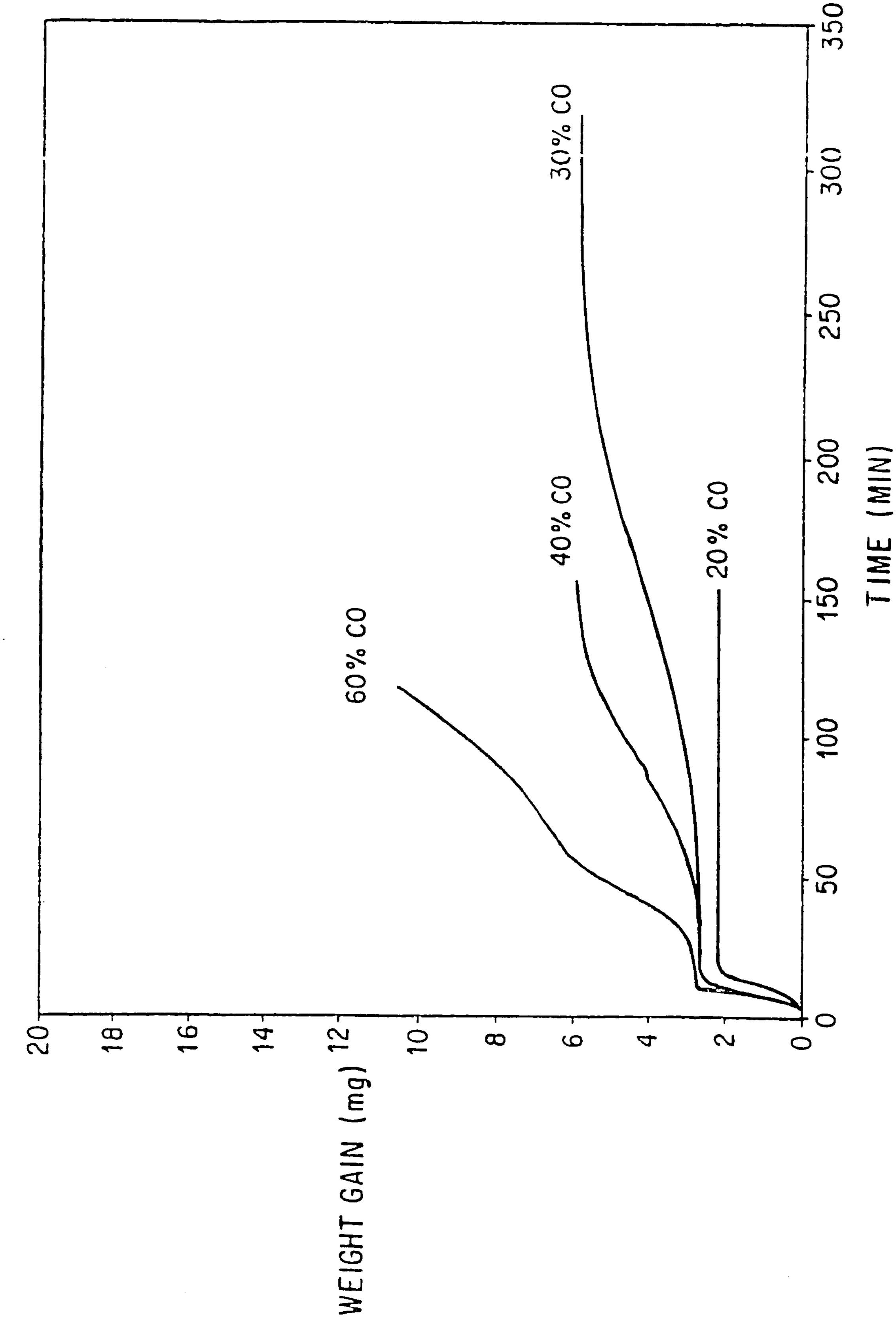

WEIGHT GAIN (mg)
TIME (MIN)
60% CO
40% CO
30% CO
20% CO
0
2
4
6
8
10
12
14
16
18
20
0
50
100
150
200
250
300
350

FIG. 8

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 92/06466

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC5: C 01 B 31/34, C 22 C 29/02

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
IPC5	C 01 B; C 22 C

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category *	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
X	US, A, 2160670 (MARCEL OSWALD) 30 May 1939, see column 2, line 46 - column 4, line 16	1,2,6,7, 8,10,13, 21,22
A		3-5,9, 11,12, 14-20
	--	
X	US, A, 3077385 (W.L. ROBB) 12 February 1963, see column 1, line 67 - column 2, line 33; column 4, line 69 - column 5, line 31; column 5, line 48 - line 56	1,6,9, 13,21
A		2-5,7,8, 10-12, 14-20, 22
	--	

* Special categories of cited documents: [10]

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed
- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step
- "Y" document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
10th November 1992	26 NOV 1992
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	Nils Engnell

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
Y	WO, A1, 9107244 (PROCEDYNE CORP.) 30 May 1991, see page 6, line 23 - page 9, line 13	1-22
Y	EP, A1, 0292195 (EXXON RESEARCH AND ENGINEERING COMPANY) 23 November 1988, see page 3, line 10 - line 46; page 4, line 8 - page 5, line 44	1-22
Y A	US, A, 4579713 (ROY C. LUETH) 1 April 1986, see column 2, line 29 - column 3, line 16; column 6, line 60 - line 68	1,6,8, 13,21, 22 2-5,7,9-12,14-20
X A	US, A, 2176802 (JOHAN ROMP) 17 October 1939, see the whole document	2,8 1,3-7,9-22
A	US, A, 3932594 (FRANK P. GORTSEMA) 13 January 1976, see column 5, line 10 - line 63	1-22
A	DE, A1, 3830111 (DORNIER GMBH) 15 March 1990, see the whole document	1-22

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.PCT/US 92/06466

SA 63328

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 30/09/92
The European Patent office is in no way liable for theseparticulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A- 2160670	30/05/39	FR-A-	833555	00/00/00
		GB-A-	516227	00/00/00
US-A- 3077385	12/02/63	NONE		
WO-A1- 9107244	30/05/91	AU-D-	6903091	13/06/91
		EP-A-	0452480	23/10/91
		JP-T-	4502650	14/05/92
EP-A1- 0292195	23/11/88	AU-B-	618262	19/12/91
		AU-D-	1648888	24/11/88
		JP-A-	1073033	17/03/89
		US-A-	4851041	25/07/89
US-A- 4579713	01/04/86	NONE		
US-A- 2176802	17/10/39	NONE		
US-A- 3932594	13/01/76	AU-D-	7551074	20/05/76
		BE-A-	823944	27/06/75
		CH-A-	600976	30/06/78
		DE-A-B-C	2461142	03/07/75
		FR-A-B-	2256106	25/07/75
		GB-A-	1500700	08/02/78
		JP-C-	990966	18/03/80
		JP-A-	50097505	02/08/75
		JP-B-	54027845	12/09/79
		NL-A-	7416954	01/07/75
		SE-B-C-	412872	24/03/80
		US-A-	4190439	26/02/80
DE-A1- 3830111	15/03/90	NONE		

For more details about this annex : see Official Journal of the European patent Office, No. 12/82